Paper electrophoresis studies showed that 2-nitroinosine exists as an anion at pH values above 4. It migrated at the same rate as xanthosine in glycine buffer at pH 9. Its mobility was enhanced to the same extent as xanthosine by the use of borate buffer at that pH. An aqueous solution of I was decolorized instantly by the addition of sodium hydrosulfite. Two products were produced. One was identified as guanosine, as it coincided with guanosine with respect to the following properties: λ_{max} 250:260 and 280:260 ratio at pH 1, 7, and 11 in the ultraviolet[9]; chromatographic mobility on paper in isobutyric acid–ammonia–water, 66:5:29 (R_f 0.50), and in water (R_f 0.59); electrophoretic mobility in borate buffer, pH 9.1. The other substance (R_f in water 0.88) has an ultraviolet spectrum similar to guanosine but has not yet been identified.

2-Nitroinosine is apparently the first published example of a pyrimidine or purine with a nitro group substituted in an electron-deficient position (2, 4, or 6).[10] It was presumably formed by nucleophilic displacement of a diazonium group by nitrite ion. Several 2-halopyrimidines and purines have been prepared by analogous processes.[11] The acidic dissociation of 2-nitroinosine is an unusually strong one for a heterocyclic ring proton. It is 3×10^5 times as strong as inosine, from which it is formally derived by replacement of a hydrogen by a nitro group. For purposes of comparison it may be noted that the introduction of a nitro group into the 5-position of uracil increases the acidity of that compound by 10^4.

It seems likely that the replacement of the guanine amino group by a nitro group occurs to some extent when nucleic acids are treated with nitrous acid. It is understandable that this product was not observed by Schuster, et al.,[3,7] as it would have been destroyed during the acidic hydrolysis used in their procedures. I is not formed in sufficient amounts, however, to account for all of the loss of guanine observed by Schuster and Wilhelm,[7] nor does the structure of I afford an explanation for the observed cross-linking of DNA. It may be that the cross-linking is due to a subsequent reaction of I. An alternative explanation would be that, within the double helix of DNA, nucleophilic displacement of the diazonium ion occurs, but that this is done by a group which is held by hydrogen bonding in the vicinity of the amino group of guanine. An obvious candidate for this role would be the 2-carbonyl group of cytosine, whose ability to participate in intramolecular nucleophilic displacements has been well documented.[12]

(9) E. A. Johnson in "The Nucleic Acids," E. Chargaff and J. N. Davidson, Ed., Vol. 1, Academic Press, New York, N. Y., 1955, p. 508.

(10) Several 8-nitropurines have been prepared: J. W. Jones and R. K. Robins, *J. Am. Chem. Soc.*, **82**, 3773 (1960).

(11) (a) I. C. Kogon, R. Minin, and C. G. Overberger, *Org. Syn.*, **35**, 34 (1955); (b) J. A. Montgomery and K. Hawson, *J. Am. Chem. Soc.*, **82**, 463 (1960).

(12) V. M. Clark, A. R. Todd, and J. Zussman, *J. Chem. Soc.*, 2952 (1951).

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Preparation of Optically Active Polyhedral Borane Derivatives

Sir:

$B_{10}H_{10}^{2-}$ has been shown to undergo a wide variety of substitution reactions,[1-5] some of which have led to apically substituted products[1,3] and others of which have led to equatorially substituted products.[4,5] Those reactions which appear to be electrophilic substitutions on $B_{10}H_{10}^{2-}$ are of special interest because the prediction has been made,[6] based on LCAO–MO calculations, that electrophilic substitution reactions on $B_{10}H_{10}^{2-}$ will occur preferentially at an apical position.

We report herein the synthesis, by means of electrophilic substitution reactions, of an equatorially substituted derivative of $B_{10}H_{10}^{2-}$, $2,7(8)-(CH_3)_3NB_{10}H_8-CO$,[7] and its resolution. This carbonyl derivative was prepared by reaction of oxalyl chloride with $2-B_{10}H_9N-(CH_3)_3^{-}$ [4] in acetonitrile at room temperature. The product was obtained as a 1:2 mixture of 2,4- and $2,7(8)-(CH_3)_3NB_{10}H_8CO(I)$ in up to 87% yield. *Anal.* Calcd. for $B_{10}H_{17}C_4NO$: B, 53.3; H, 8.45; C, 23.6; N, 6.90; mol. wt., 203. Found: B, 53.4; H, 8.44; C, 23.9; N, 6.91; mol. wt., 201. The carbonyl group of I is chemically similar to the carbonyl groups of $1,10-B_{10}H_8(CO)_2$.[3] Reaction of the carbonyl derivative, I, with hydroxylamine-O-sulfonic acid[3] followed by methylation[4] (eq. 1) gave $B_{10}H_8[N(CH_3)_3]_2$ (II)

$$(CH_3)_3NB_{10}H_8CO \xrightarrow[\text{2, }(CH_3)_2SO_4-NaOH]{\text{1, }NH_2OSO_3H} B_{10}H_8[N(CH_3)_3]_2 \quad (1)$$
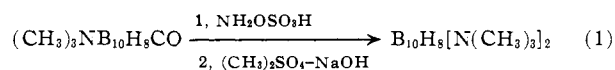
as a mixture of 2,4- and 2,7(8)- isomers as shown by X-ray comparison with authentic 2,4-[4] and 2,7(8)-[8,9] isomers of II.

Treatment of aqueous I with brucine hydrochloride gave brucine-H^+ $(CH_3)_3NB_{10}H_8COOH^-$, from which the highly soluble 2,4- isomer was removed by warm ethanol. Fractional crystallization of the remaining mixture of diastereomeric salts from ethanol–acetonitrile followed by reconversion to I gave $(+)2,7-$ (or 2,8-) $(CH_3)_3NB_{10}H_8CO$,[10] with $[\alpha]^{23}D +22°$ (c 1.8, acetone), m.p. 207–208.5°, derived from the less soluble brucine salt, and the $(-)$enantiomer with $[\alpha]^{23}D -14°$ (c 2.42, acetone) derived from the more soluble brucine salt. No observable loss of optical activity occurred on heating $(+)$-I to 200° for 5 min. Higher

(1) W. H. Knoth, H. C. Miller, D. C. England, G. W. Parshall, E. L. Muetterties, and J. C. Sauer, *J. Am. Chem. Soc.*, **84**, 1056 (1962).

(2) W. H. Knoth, H. C. Miller, J. C. Sauer, J. H. Balthis, Y. T. Chia, and E. L. Muetterties, *Inorg. Chem.*, **3**, 159 (1964).

(3) W. H. Knoth, J. C. Sauer, H. C. Miller, and E. L. Muetterties, *J. Am. Chem. Soc.*, **86**, 115 (1964).

(4) W. R. Hertler and M. S. Raasch, *ibid.*, in press.

(5) W. H. Knoth, J. C. Sauer, D. C. England, W. R. Hertler and E. L. Muetterties, *ibid.*, in press.

(6) R. Hoffman and W. N. Lipscomb, *J. Chem. Phys.*, **37**, 520 (1962).

(7) The numbering system for $B_{10}H_{10}^{2-}$ which is used here is the proposed revision of the ACS Nomenclature Committee, 1963, which is described by R. Adams, *Inorg. Chem.*, **2**, 1087 (1963), see Fig. 1.

(8) W. R. Hertler, *Inorg. Chem.*, in press. $2,7(8)-B_{10}H_8[N(CH_3)_3]_2$ was prepared by the sodium–alcohol reduction of $2,7(8)-B_{10}H_8[N(CH_3)_2CH_2Cl]_2$ which was obtained from the reaction of $B_{10}H_{10}^{2-}$ with $ClCH=N(CH_3)_2^+Cl^-$. The configurational assignment is based on B^{11} n.m.r. data which, incidentally, do not rule out 2,6(9)- geometry.

(9) The stereochemical assignment for I is based on formation of 2,4-II and 2,7(8)-II and requires the assumption that no stereochemical change results from the reaction of eq. 1. There is ample support for such an assumption in the several reactions of $1,10-B_{10}H_8(CO)_2$ described in ref. 3.

(10) This appears to be the first preparation of a *stable* optically active boron compound in which the asymmetry (albeit molecular asymmetry) resides on boron. See, however, J. Böeseken and J. Meulenhoff, *Proc. Acad. Sci. Amsterdam*, **27**, 174 (1924).
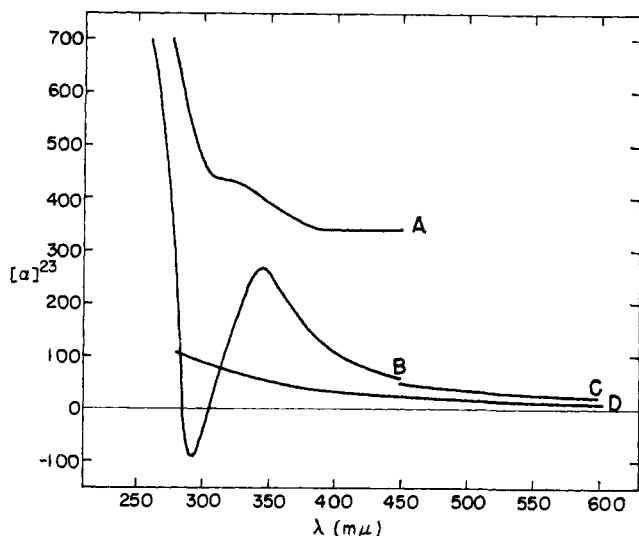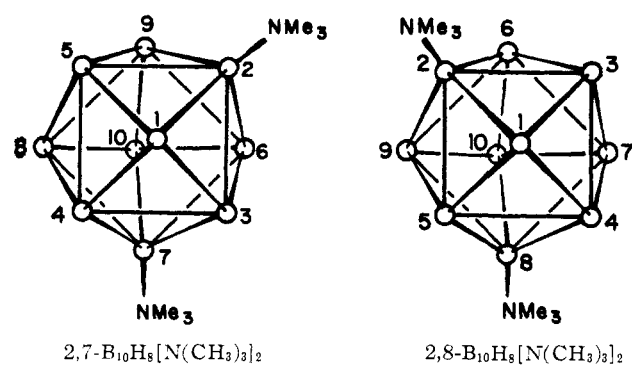
2,7-$B_{10}H_8[N(CH_3)_3]_2$ 2,8-$B_{10}H_8[N(CH_3)_3]_2$

Figure 1.

Fig. 2.—A, ultraviolet spectrum of 2,7(8)-I in methylene chloride (ϵ_{320} 540); B, ORD curve of (+)2,7- (or 2,8-) I in methylene chloride (c 0.036); C, ORD curve of (+)2,7- (or 2,8-) I in acetonitrile (c 2.5); D, ORD curve of (+)2,7- (or 2,8-) II in acetonitrile (c 2.5).

temperatures were not investigated because slow decomposition was apparent above 200°. (+)2,7- (or 2,8-) I was converted as shown in eq. 1 to (+)2,7- (or 2,8-) $B_{10}H_8[N(CH_3)_3]_2$ with $[\alpha]^{25}D$ +13° (c 1.9, acetonitrile). Figure 1 indicates the enantiomeric relationship of 2,7- and 2,8-II. The existence of (+)-$B_{10}H_8[N(CH_3)_3]_2$ (II) precludes any geometry[11] other than 2,7(8)- or 2,6(9)- for II and hence for I. 2,6(9)-geometry appears unreasonable on both steric and electronic grounds. The optical data confirm the B^{11} n.m.r. assignment for 2,7(8)-II.[8] 2,7(8)-II undergoes polyhedral isomerization[12] at temperatures in the vicinity of 300°, and details of this isomerization will be reported subsequently.

The optical rotatory dispersion (ORD) curves of (+)2,7- (or 2,8-) I and (+)2,7- (or 2,8-) II (Fig. 2) confirm the configurational relationship of the two compounds. The positive Cotton effect superimposed on the plain ORD curve of (+)2,7- (or 2,8-) I corresponds to a shoulder in the ultraviolet spectrum of I at ~320 mμ (ϵ 540) which may arise from an n → π^* transition.

(11) Of the nine possible isomers of I, three are dl- pairs, viz., the 2,3(5)-, 2,6(9)-, and 2,7(8)- isomers. Two of the seven possible isomers of II are dl- pairs, viz., the 2,6(9)- and 2,7(8)- isomers.

(12) For discussions of polyhedral isomerization processes see R. Hoffmann and W. N. Lipscomb, Inorg. Chem., 2, 231 (1963), and A. Kaczmarczyk, R. D. Dobrott, and W. N. Lipscomb, Proc. Natl. Acad. Sci. U. S., 48, 729 (1962). See also M. F. Hawthorne, R. L. Pilling, P. F. Stokely, and P. M. Garrett, J. Am. Chem. Soc., 85, 3704 (1963).

Our results show that the reaction of oxalyl chloride with 2-$B_{10}H_9N(CH_3)_3^-$ proceeds with a high specificity for equatorial substitution. However, this does not necessarily imply a higher ground state electron density at equatorial than at apical positions of the substrate. Indeed there is probably no reason to expect a priori that an orientation–electron density correlation[6] should be valid in all instances of polyhedral borane substitution, since correlation of orientation in aromatic substitution reactions with ground-state electron densities at various positions of aromatic rings is not rigorous from the viewpoint of transition-state theory.[13] In particular, the lack of knowledge of mechanistic details in electrophilic substitution reactions on polyhedral boranes makes an understanding of orientation effects in these reactions exceedingly difficult.

Acknowledgment.—The author gratefully acknowledges the determination of the ORD curves by Dr. V. E. Shashoua.

(13) See, for example, J. Hine, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1956, p. 351, and references cited therein.

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Isoracemization of Trialkylammonium Carbanide Ion Pairs[1]

Sir:

Previous publications have reported results of investigations of the base-catalyzed isotopic exchange reaction of carbon with oxygen acids. The stereochemistry of the reaction was derived from the relative exchange (rate constant k_e) and racemization (rate constant k_α) rates. Values of the ratio k_e/k_α have been obtained which indicate that electrophilic substitution can occur with retention ($k_e/k_\alpha \gg 1$), complete racemization ($k_e/k_\alpha = 1$), or inversion ($k_e/k_\alpha = 0.5$ to 1).[2] We now report k_e/k_α values which are less than 0.5, and evidence for occurrence of a base-catalyzed intramolecular racemization reaction is presented.

Compounds I and II were prepared by conventional reactions in optically active form with and without deuterium in the indicated positions.[3] Table I records the results of the exchange–racemization experiments, as well as the reaction conditions and physical properties of the two substrates.

Id

IId, X = NO₂
IIId, X = H
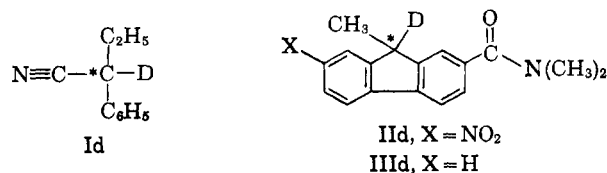
(1) This work was supported by a grant from the Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgment is hereby made to donors of this fund.

(2) D. J. Cram and L. Gosser, J. Am. Chem. Soc., 85, 3890 (1963), and earlier papers.

(3) Elemental analysis of all new compounds gave values within 0.3% of theory, whereas the physical properties of known compounds correspond to literature values.